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APO, A VERSATILE TEXTILE CHEMICAL

Literature Review with Bibliography

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APO - A VERSATILE TEXTILE CHEMICAL
Literature Review with Bibliography

by

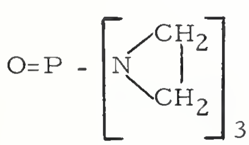
R. M. Perkins, G. L. Drake, Jr., and W. A. Reeves

The quest for new cellulose reactants and other textile finishes has led to the use of a trifunctional phosphorus compound, $C_6H_{12}N_3OP$, tris(1-aziridinyl) phosphine oxide, often referred to as APO.

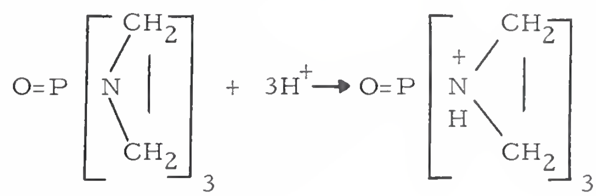
APO can be made in good yield by the reaction of phosphorus oxychloride with ethylenimine, using an acid acceptor like triethylamine in some inert solvent such as benzene (6).[1]

APO is soluble in water and in most common organic solvents, with a limited solubility in petroleum ether. Other physical properties are: molecular weight, 173.2; melting point, 43.5° C; boiling point decomposes. It is usually sold commercially as an 80 to 90 percent alcoholic solution. APO and its solutions, which are inclined to polymerize, can be stabilized by the addition of anhydrous methanol, ethanol, peroxides or dehydrating compounds (11, 12).

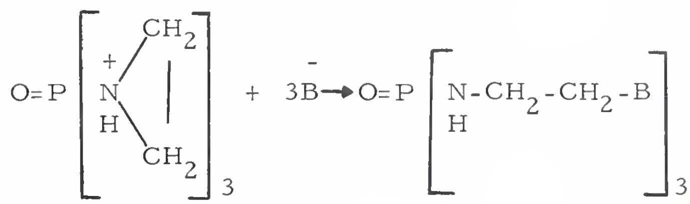
Because it contains three aziridine rings,



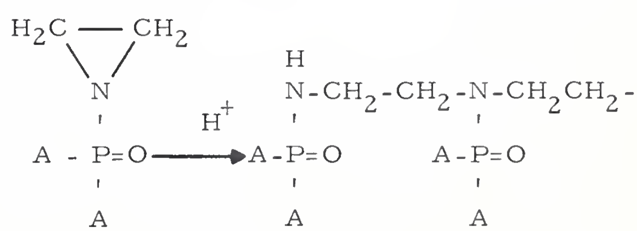
APO is a very reactive chemical, which undergoes addition and polymerization reactions via ring opening. Under acid conditions, the reaction is believed to occur in two steps: the first involves the formation of an immonium ion by protonation.



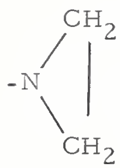
In the second step, the ring is opened by a suitable nucleophilic agent ($\bar{B}$) yielding the addition product:



By using modern polargraphic techniques, it is shown that a N-C bond of the ethyleneimine ring, protonized in a preceding reaction, is split (62). In an acid solution, APO will homopolymerize or copolymerize with other aziridine compounds.

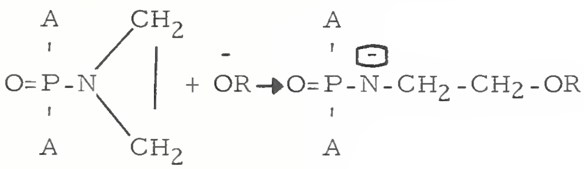


[1]Figures in parentheses refer to Bibliography at end of publication.

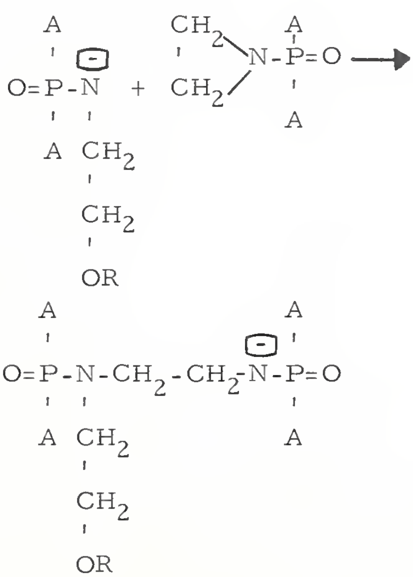
where A is 

In actual practice, polymerization involves all of the aziridine rings of the molecule, and a highly crosslinked polymer results.

In basic media, the reaction is thought to involve the attack of the nucleophile on the ring carbon giving rise to an amide ion.



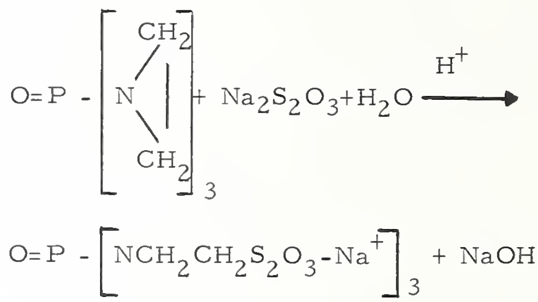
R can represent cellulose, and in the case of reaction with more than one aziridine ring, crosslinking can occur. A proposed mechanism for polymerization is as follows:



This negatively charged nitrogen atom can open another aziridine ring, or, since the reaction is carried out in aqueous solution, be protonated by a hydrogen ion from a water molecule. The overall rate of this reaction is considerably slower than the acid catalyzed process.

Opening of the aziridine ring may also occur under neutral conditions. The reaction mechanism is not clear and the reaction rate is slower than either the acid or base catalyzed process.

Ring opening is the basis for the assay of imine rings by the methods of both Schaefer (56), and of Allen and Seaman (4). The methods are based on a rapid reaction between the ethyleneimino group and sodium thiosulfate under acid conditions. In the method



of Allen and Seaman, the sodium hydroxide is neutralized by a predetermined excess of acid. Back titration of this acid determines the number of equivalents of sodium hydroxide released, and this is equal to the number of equivalents of imine rings. In Schaefer's method the unreacted sodium thiosulfate is titrated with iodine to demonstrate the extent of the reaction.

Two qualitative tests have been developed by the Quartermaster Laboratory at Natick. One test is for the identification of durable flame-resistant finishes (31), and the other is a test for distinguishing APO from THPC (tetrakis(hydroxymethyl)phosphonium chloride) on APO-THPC treated fabric (32).

When APO is applied to cellulosic materials, it can react with the cellulose, condense with itself to form a polymer, or react with other active substituents to form copolymers. APO has been used alone or with a coreactant as a flameproofing finish. It has

been used to produce a wash-wear cotton with excellent smooth drying and crease resistant properties; a durable embossed pattern; a multipurpose finish; and as a binder in pigment printing and dyeing.

APO AS A FLAME-RETARDANT FINISH

In 1957, Reeves, et al. (45), first described the use of APO, in combination with tetrakis (hydroxymethyl)phosphonium chloride (THPC) as a durable flame-retardant finish for cotton materials. In addition, the treated fabrics were resistant to rot and mildew. Two U. S. patents, 2,886,539 (17) and 2,911,325 (18), and one British patent 837,709 (2), describe flame-resistant polymers and textiles using APO or APS (tris(1-aziridinyl)phosphine sulfide) with THPC or THPO (tetrakis(hydroxymethyl)phosphine oxide). Drake and coworkers give processing details for treating textiles with APO-THPC (13, 14). The U. S. Naval Air Development Center (60), and the U. S. Army Headquarters Quartermaster Research and Engineering Command (34) have evaluated APO-THPC treated fabrics for military combat and flight suits. The use of APO with THPC as a flame-retardant finish has been reviewed by several authors (20, 36, 58).

In addition to the reaction with THPC to impart flame resistance, APO can be used with other agents. Considerable work in this area has been done at the Southern Regional Research Laboratory. Reeves and his coworkers have been issued patents covering APO with organic amino compounds (42, 43); with active methylene groups (44); with phenols (49); with carboxylic acids (46); with polyhydric alcohols (7, 8); and as a copolymer with APS (9) or without a coreactant (10). APO has also been used to modify carboxyalcyl cellulose textiles (50) and phosphonomethylated cotton sheeting (47), thereby imparting flame resistance. Other workers have used APO with a coreactant for flame-retardant textiles and these are described in British patents 837,710 (2), and 903,820 (51); French patent 1,322,330 (57); and U. S. patents 3,034,919 (59) and 3,085,029 (35). For the Office of the Quartermaster General, the University of Rhode Island studied the use of APO, and analogues of APO, with melamine-formaldehyde as a flame retardant (61). With an acid catalyst, such as $Zn(BF_4)_2$, APO can impart flame retardancy to cotton without a coreactant (15). An infrared technique for the rapid screening of catalysts for the polymerization of APO is described by Miles and Hoffman (33). Frieser reviewed the use of APO, as well as other durable flame-retardant formulations, in his "Fundamentals and Methods in Flameproofing of Textiles" (19).

APO AS A WASH-WEAR FINISH

APO as a wash-wear finish for cotton was studied extensively by Drake and Guthrie (15). With $Zn(BF_4)_2$ as the preferred catalyst, samples were prepared with over 300° crease-recovery angles (Monsanto method). APO treated fabrics also exhibit excellent muss-resistant properties. The finish could not be stripped from the fabric by methods that are effective with most other resins. Recent work of the Southern Laboratory and of industry has been expanded to include pilot-plant and mill operations. In an article appearing in Melliand Textilber, APO is described as the most satisfactory compound for producing the best dry- and wet-crease recovery cellulosic textiles (1).

If APO-finished white fabric is given a chlorine bleach, it yellows. This discoloration can be reduced to below noticeable

levels by means of peroxide and perborate bleaching, and by various other means (29), but the discoloration reappears when the fabric is aged or when it is retreated with a chlorine bleach.

Both partially carboxymethylated cotton (52), and carboxyalkyl cellulose (50) show some improvement in crease recovery after further treatment with APO. A review of the chemistry of thermosetting resins and related compounds by Smith includes APO as a creaseproof finish, and in combination with other compounds as a flameproof finish (58). British patent 906, 324 (23) describes radiation curing of APO precondensates in cellulosic textiles.

APO AS A MULTIPURPOSE FINISH

Recent developments in textile finishing have included the application of more than one improved and desirable property to the cotton material from a single formulation. For example, it is possible to dye a fabric or render it oil or water repellent while simultaneously crosslinking the cellulose for wash-wear properties. Since APO is a trifunctional compound, it is ideal for multiple finishes. It can theoretically crosslink cotton and at the same time have a free aziridinyl group to react with another compound having an active hydrogen, thereby indirectly attaching this other compound to the cellulose. Halotriazine dyes have been successfully attached to cotton with APO, and this technique has been patented by Reeves, et al (48). This method of simultaneously attaching dyes while rendering the textile fabric wrinkle resistant, in both laboratory and pilot plant applications, was reported by Perkins and coworkers (39). A study was made comparing the effectiveness of APO as a multipurpose finish with a difunctional aziridinyl compound and a hexafunctional aziridinyl compound (38). A recent article reported the use of APO in producing durably embossed cotton textiles. Fabric was dyed, embossed, and given a wash-wear finish in a single operation with pilot plant equipment (37). At the Southern Regional Research Laboratory an investigation is being conducted to attach various hydrophilic and hydrophobic groups, molecules or polymers, to cellulose with APO.

APO IN PIGMENT DYEING AND PRINTING

Small quantities of APO (and other ethyleneimine derivatives) have been successfully used for the attachment of pigments to cellulosic materials. Examples of the use of APO for pigment attachment can be found in German patents 914, 123 (41) and 1, 060, 350 (64), and Belgium patent 613, 442 (30). Improved pigment adhesion is also the subject of German patent 1, 044, 761 (25) and British patent 877, 865 (26). Russian patent 115, 470 (28) claims an increased fastness of acid dyes if, prior to dyeing, the fibers of animal origin are steeped in aqueous solutions of APO; and Japanese patent 7, 685 (53) reports improved dyeability with acid, direct or basic dyes, if the cellulosic fibers are first treated with phosphoric acid monoethylenimide derivatives. Another Japanese patent 8, 492 (54) claims increased dye affinity of poly (vinyl alcohol) fibers by using APO.

RELATED PUBLICATIONS

German patent 1,023,446 (21) describes the use of polyfunctional ethylenimine compounds in the stiffening and dressing of hats and felts. Derivatives of ethylenimine are recommended as stabilizers for polymers, especially acid producing polymers like poly(vinyl chloride) (27, 40). Two U.S. patents 2,911,321 (24) and 2,949,393 (3), and one Japanese patent 8,192 (55), describe the use of APO as a bonding or anchoring agent. Interchemical Corporation prepared water- and heat-resistant vinyl-latex adhesives with a small amount of MAPO (tris (1-(2-methyl)aziridinyl)phosphine oxide) (22).

A paper on skin tests of flame-retardant materials, including APO, was published by the Western Utilization Research and Development Division (63), and on the physiological and biological properties of APO and APS cotton flame retardants by the Southern Utilization Research and Development Division (16). Samples of APO-THPC cotton poplin were pyrolyzed in a helium stream by exposure to flux levels of 5-25 cal./sq. cm-sec. for 1 sec. in a carbon arc imaging furnace (5).

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